PB87-105540

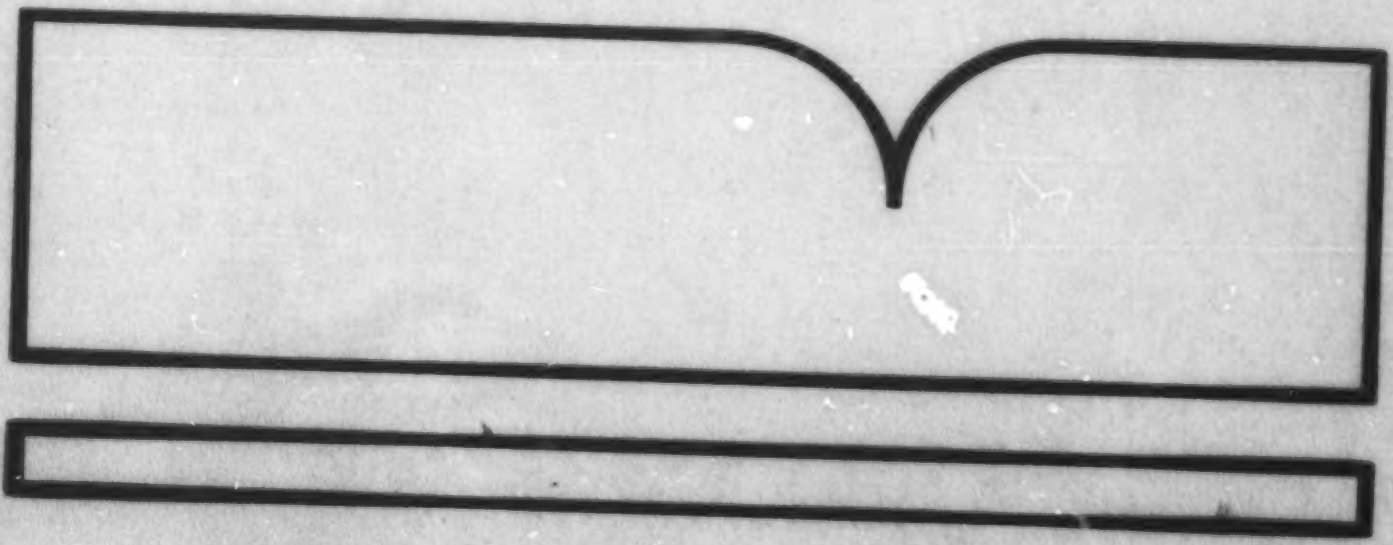
Novel Precursor of Trihalomethanes

(U.S.) Environmental Protection Agency
Cincinnati, OH

Prepared for

Electric Power Research Inst., Palo Alto, CA

1986



[redacted]

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RE PB87-105540
EPA/600/D-86/224		

4. TITLE AND SUBTITLE	5. REPORT DATE
NOVEL PRECURSOR OF TRIHALOMETHANES	October 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
W.J. Cooper and D.M. Kaganowicz	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Florida Internat'l University, Miami, FL 33199	
	11. CONTRACT/GRANT NO.
	CR 810277-01
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Water Engineering Research Laboratory- Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	Published Paper
	14. SPONSORING AGENCY CODE
	EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer: A. Stevens, 513/569-7342 In: Water Chlorination: Chemistry, Environmental Impact and Health Effects (Vol. 5), Williamsburg, VA, 6/3-8/84, pp. 895-906.

16. ABSTRACT
To optimize water treatment processes, a better understanding of the mechanisms and factors affecting the formation and distribution of trihalomethanes (THMs) is needed. Recent studies indicate that α-methylbenzylamine (α-MBA) can act as a precursor for THMs. This chapter discusses the formation of THMs as a function of the variables, bromide and pH at a chlorine to α-MBA mole ratio of 1.0. The formation curves for the total THM as carbon closely follow those of natural waters, indicating that α-MBA is a good candidate for studying THM formation rates.

(Copyright by ...)

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	15
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.

EPA/600/D-86/224
October 1986

WATER CHLORINATION

Chemistry, Environmental Impact and Health Effects

Volume 5

Edited by
Robert L. Jolley
Richard J. Bull
William P. Davis
Sidney Katz
Morris H. Roberts, Jr.
Vivian A. Jacobs

Proceedings of the Fifth Conference on
Water Chlorination: Environmental Impact and Health Effects
Williamsburg, Virginia
June 3–8, 1984

Sponsored by
Electric Power Research Institute, National Cancer Institute,
Oak Ridge National Laboratory, Tennessee Valley Authority,
U.S. Department of Energy, U.S. Environmental Protection Agency,
Virginia Institute of Marine Science–School of Marine Science, and
College of William and Mary

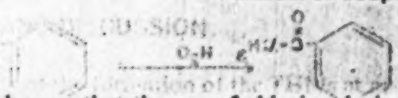
LEWIS PUBLISHERS, INC.

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

CHAPTER 70

Novel Precursor of Trihalomethanes

William J. Cooper and Della M. Kaganowicz



It is well known that the use of chlorine during water treatment produces trihalomethanes (THMs) in the presence of natural aquatic humic substances.[1] It is also known that there is considerable variability in the chemical nature of humic material and this variability can give rise to different THM formation potentials.[2,3] To gain a better understanding of the chemical reactions that occur when chlorine is added to waters containing natural aquatic organics, some research has focused on the use of model organic compounds (i.e., model precursors) with structures similar to those in natural aquatic humic substances such as aromatic polyhydroxy compounds[4-12] and other compounds.[11-14]

There are probably numerous precursor molecules having diverse functional groups of natural origin.[11] This observation is supported in part by the relatively elusive structure of naturally occurring humic and fulvic acids, the apparent long reaction times observed in natural waters (assuming an excess chlorine), and experimental work with model compounds of diverse structure. Although several mechanisms could lead to the formation of THMs, the relative significance of the mechanisms is not known. It is possible that all are operative to a greater or lesser extent in the formation of THMs in natural waters.

Our recent studies indicate that α-methylbenzylamine can act as a precursor for THMs. The overall mechanism can be divided into two series, the first producing acetophenone and the second, the classical haloform reaction, forming THMs and benzoic acid (Figure 1). The first series of reactions, resulting in the formation of acetophenone, was reported using phase transfer catalysis.[15] We have studied the formation of THMs when aqueous solutions of α-methylbenzylamine (α-MBA) are chlorinated.

This chapter discusses the formation of the trihalomethanes as a function of the variables, bromide and pH at a chlorine (Cl_2) to α-MBA mole ratio of 1.0. These results serve as a model for THM formation in natural waters and may contribute to a better understanding of the effect of bromide in natural waters and the formation and distribution of trihalomethanes.

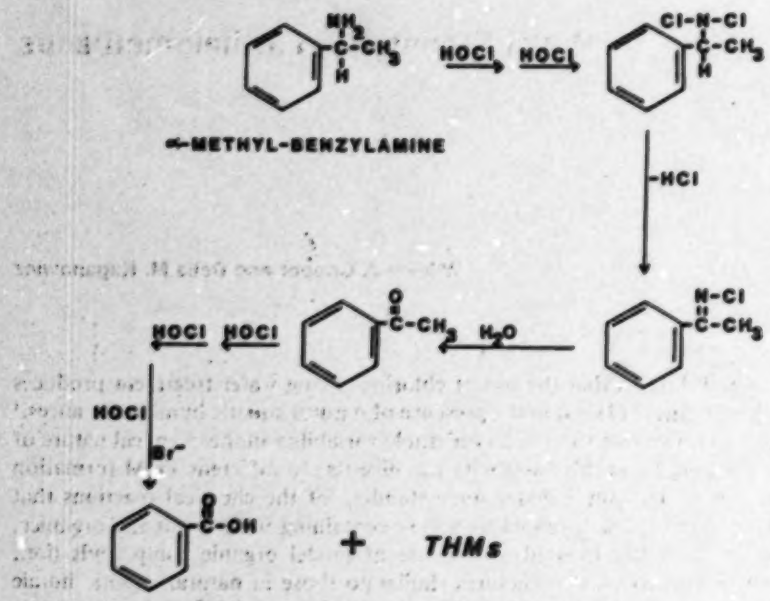


Figure 1. Reaction pathway of α-methylbenzylamine and HOCl.

EXPERIMENTAL

The formation and distribution of the four chlorinated and brominated THMs were studied at a precursor (α-MBA) concentration of 10^{-4} *M*. The concentration of Cl_2 was also held constant at 10^{-4} *M*, while Br^- and pH were varied.

All experiments were conducted in chlorine-demand-free water.[16] Sufficient bromide was added as KBr (infrared grade) to give final concentrations of 1×10^{-4} *M* (8.0 mg/L Br^-), 1×10^{-5} *M* (0.8 mg/L Br^-), and 1×10^{-6} *M* (0.08 mg/L Br^-). Chlorine solutions were prepared from a NaOCl solution (Fisher Reagent Grade) and standardized using iodometric titration.[17] Chlorine concentrations during the reactions were determined using a continuous total chlorine analyzer (CHLORTECT®, EPCO, Woodburry, Connecticut).[18] After chlorine was added to the samples, the reaction was allowed to proceed for 2, 6, 24, 72, and 144 h in the dark. For any one reaction series, sodium thiosulfate (0.1 g/60-mL sample) was added to stop any further reaction at the predesignated times. The samples were then stored in the refrigerator (4°C) in 60-mL serum vials with Teflon®-lined silicon septa secured with aluminum crimp-topped seals until THM analysis. (In no case were the samples stored for more than

more than 10 d). In separate experiments we have shown that the THMs are invariant in concentration for at least 60 d when stored under the conditions used in this experiment.) To adjust the pH of the samples at 5.0, 7.0, 9.0, and 11.0, we used KH_2PO_4, K_2HPO_4 + KH_2PO_4, $Na_2B_4O_7$, and Na_2CO_3 at 0.01 *M*, respectively. THMs were determined by liquid-liquid extraction[19] followed by gas chromatography using a Hall electrolytic conductivity detector (Tracor Model 700).

RESULTS AND DISCUSSION

The results of the formation of the THMs at an α-MBA/Cl_2 mole ratio of 1 and Br^- concentration of 10^{-4} *M* are shown in Figure 2. The total chlorine concentration was measured at each reaction time and is also presented. It was observed that at every pH except 5, $CHCl_3$ was the predominant THM formed and increased in concentration with time. Bromoform was either below the detection limit or detected only at trace levels at pH 5 and 7. At pH 9 and 11, $CHBr_3$ was observed but only at low concentrations. The concentration of the total THMs (THMs as carbon, THM-C) increased with time and pH. The increased pH appeared to favor the formation of $CHCl_3$. The THM-C data are summarized in Figure 3. From this it appears that at a Br^- concentration of 10^{-6} *M*, the formation of the THMs, as moles per liter of carbon, is approximately linear on a log-log plot of THM-carbon concentration vs OH^- concentration, at all reaction times.

The results of the formation of THMs at a Br^- concentration of 10^{-5} *M* are presented in Figure 4. At pH 5 and 7 the predominant THM formed was $CHCl_2Br$, whereas at pH 9 the $CHClBr_2$ predominates slightly over the $CHCl_2Br$. At pH 11, initially the more brominated THMs, $CHClBr_2$ and $CHBr_3$, predominated. The formation of $CHBr_3$ was essentially complete within 6 h, whereas the formation of $CHClBr_2$ reached a plateau (minimal additional increase in concentration) after 24 h. At this time, the Br^- had all been converted into organic bromine. With excess chlorine the chlorinated THMs, $CHCl_2Br$ and $CHCl_3$, began to increase significantly until at 144 h the $CHCl_3$ was the predominant THM formed, representing 56% of the total THM-C.

At pH 5, $CHBr_3$ was observed as only a trace ($< 10 \times 10^{-9}$ *M*). As the pH of the reaction was increased, $CHBr_3$ was formed; at pH 7, it reached concentrations that could be quantitated only after 72 and 144 h. At pH 9, $CHBr_3$ formed rapidly and in a higher concentration than $CHCl_3$, but less than the mixed halogen species. The formation of $CHBr_3$ at pH 11 was extremely rapid and appeared to reach maximum concentration after 6 h reaction time.

Figure 5 summarizes the formation of the THMs at Br^- concentration of 10^{-5} *M*. The formation of the THM-C is again approximately linearly related to OH^- concentration (when plotted as log-log).

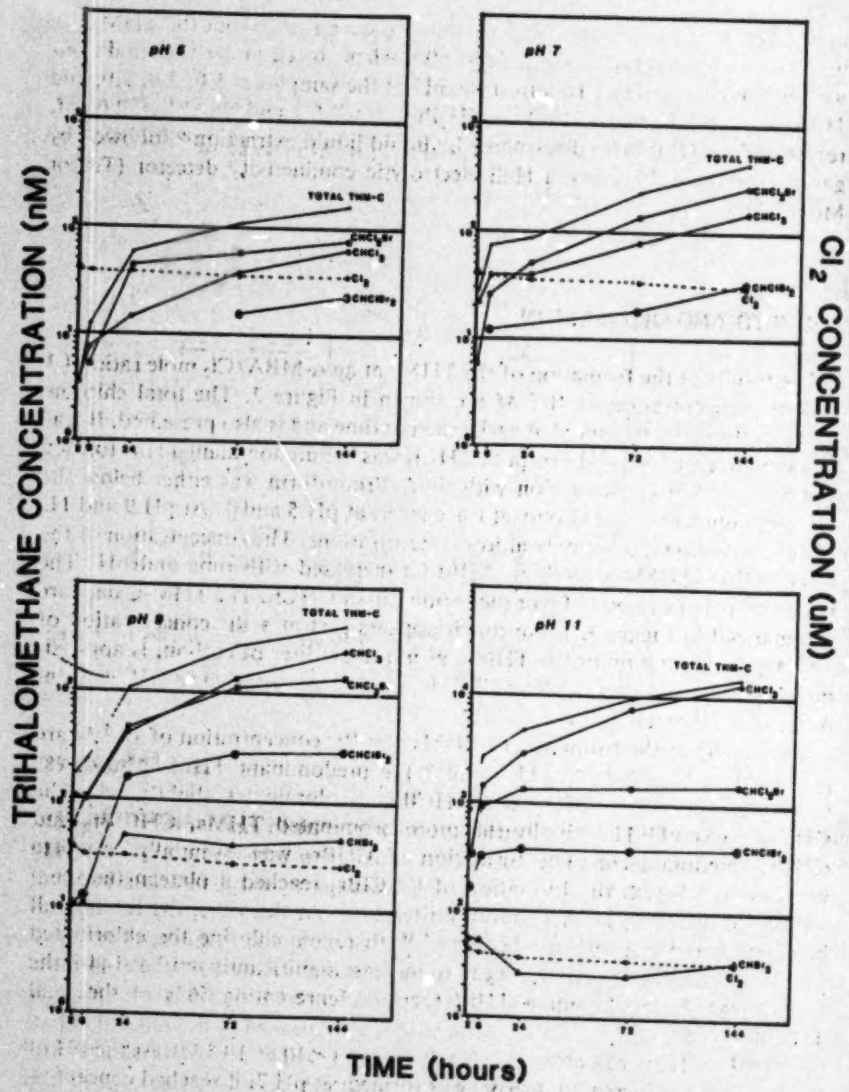


Figure 2. Trihalomethane formation at an α-methylbenzylamine/Cl_2 mole ratio of 1 and Br^- = 10^{-6} *M*.

The results of the formation of the THMs at Br^- concentration of 10^{-4} *M* are presented in Figure 6. In this experiment the α-MBA, Cl_2, and Br^- concentrations were all 10^{-4} *M*. At almost every pH and reaction time, $CHBr_3$ is the predominant THM. At pH 5, $CHCl_3$ is formed at concentrations greater than

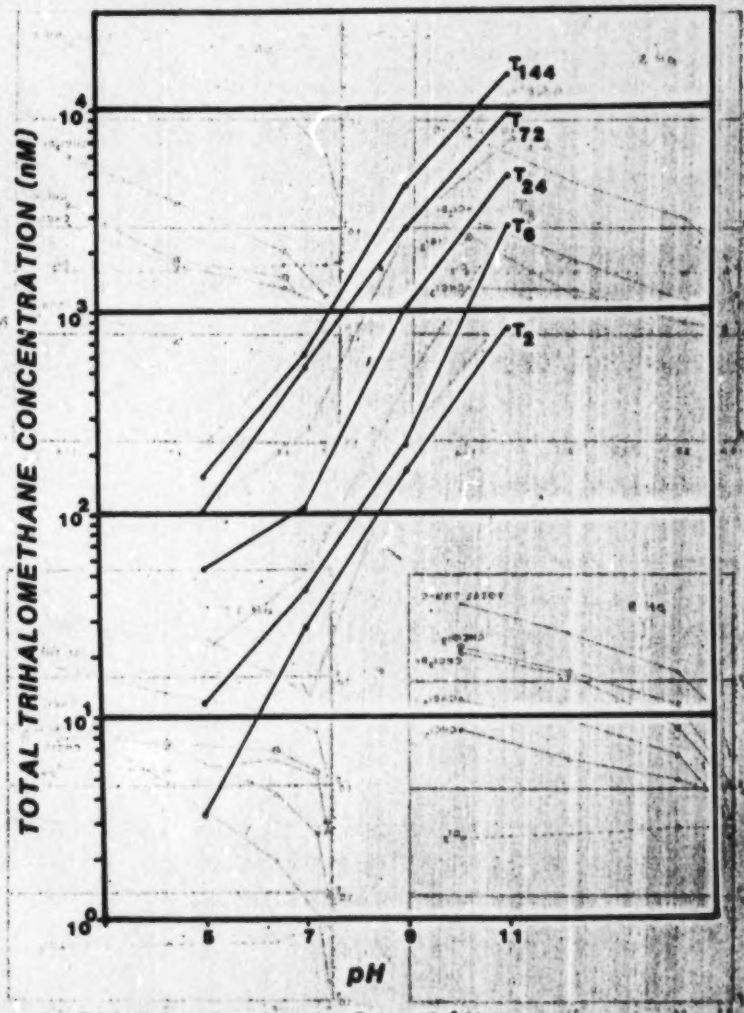


Figure 3. Total trihalomethane formation, Br^- = 10^{-6} *M*.

the mixed halogen THMs. The increase in pH favored the formation of the $CHClBr_2$ and $CHBr_3$. The concentrations of $CHBr_3$ and $CHClBr_2$ both increased with time and pH, as did the total THM concentration as carbon. Figure 7 shows the result of the THM-C concentration at different reaction times and pH. The THM-C concentration appeared to decrease at pH 7 when compared with that at both pH 5 and 9. This effect is not understood as yet but indicates that, at this concentration of Br^- (10^{-4} *M*), an acid/base catalyzed step was rate limiting (i.e., slowed down THM formation).

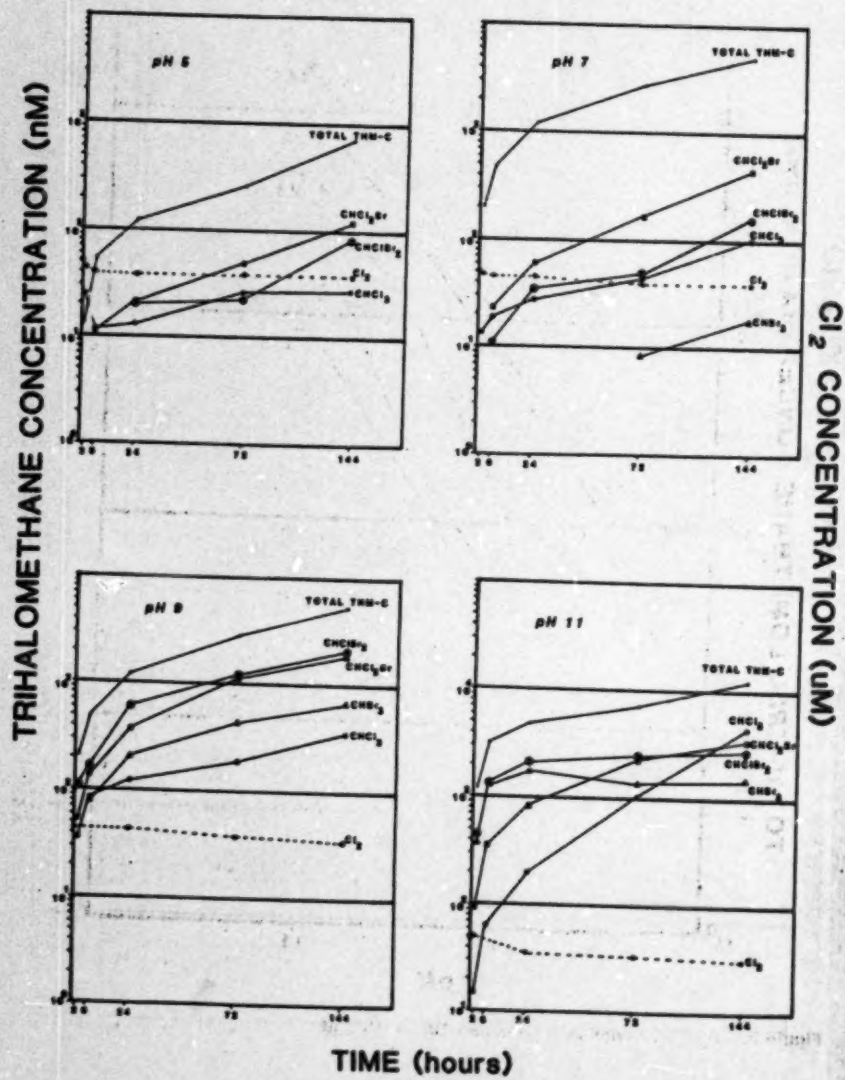


Figure 4. Trihalomethane formation at an α-methylbenzylamine/Cl_2 mole ratio of 1 and Br^- = 10^{-5} *M*.

It has been reported that, in general, when Br^- is present, the molar concentration of the THMs increases.[4,6,7] By comparing the results of the total THM-C curves in the above figures, it can be seen that in this study, the addition of Br^- did not increase the total THM-C concentration. At pH 5, 10^{-5} *M* Br^- increased the total THM-C relative to the samples containing 10^{-6} and 10^{-4} *M*

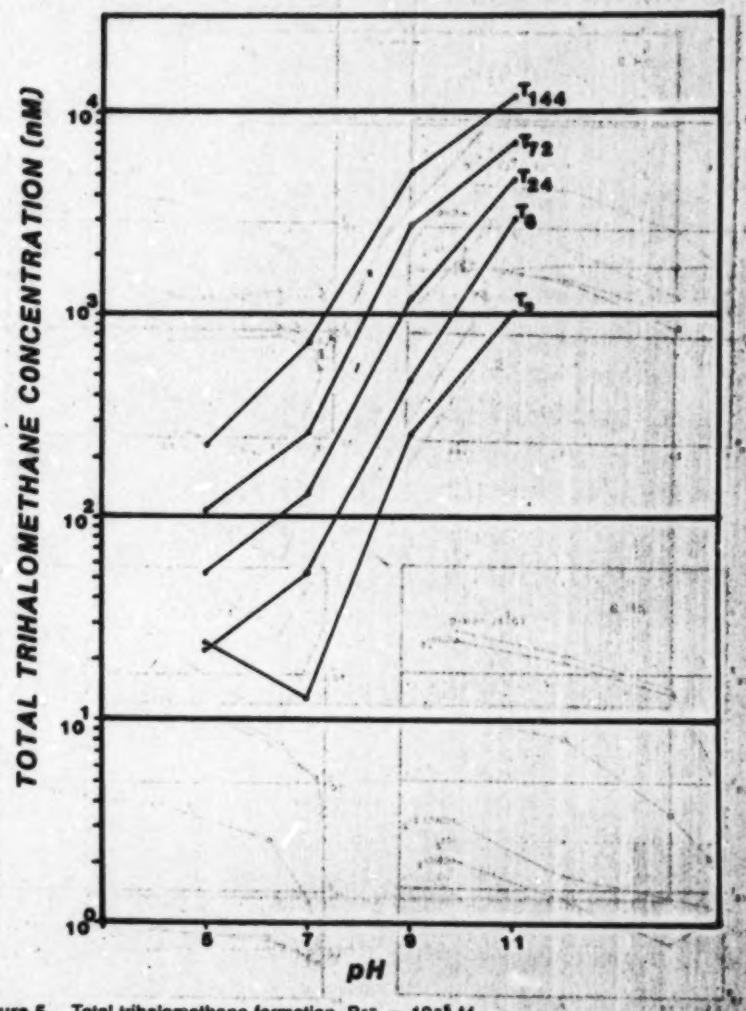


Figure 5. Total trihalomethane formation, Br^- = 10^{-5} *M*.

Br^-. At pH 9, the total THM-C concentration is similar at the two lower Br^- concentrations; however, when Br^- was added (10^{-4} *M*), the concentration of total THM-C decreased by approximately 50% at 144 h reaction time. The Br^- concentration had little effect on the formation of total THM-C at pH 11.

Amy et al.[20] studied the effect of Br^- on the formation and distribution of THMs in natural waters. They found that as the pH increased the relative conversion of Br^- to THM-Br also increased. We found that at a reaction time of 144 h and pH 5, 7, and 11 the relative conversion of Br^- to THM-Br

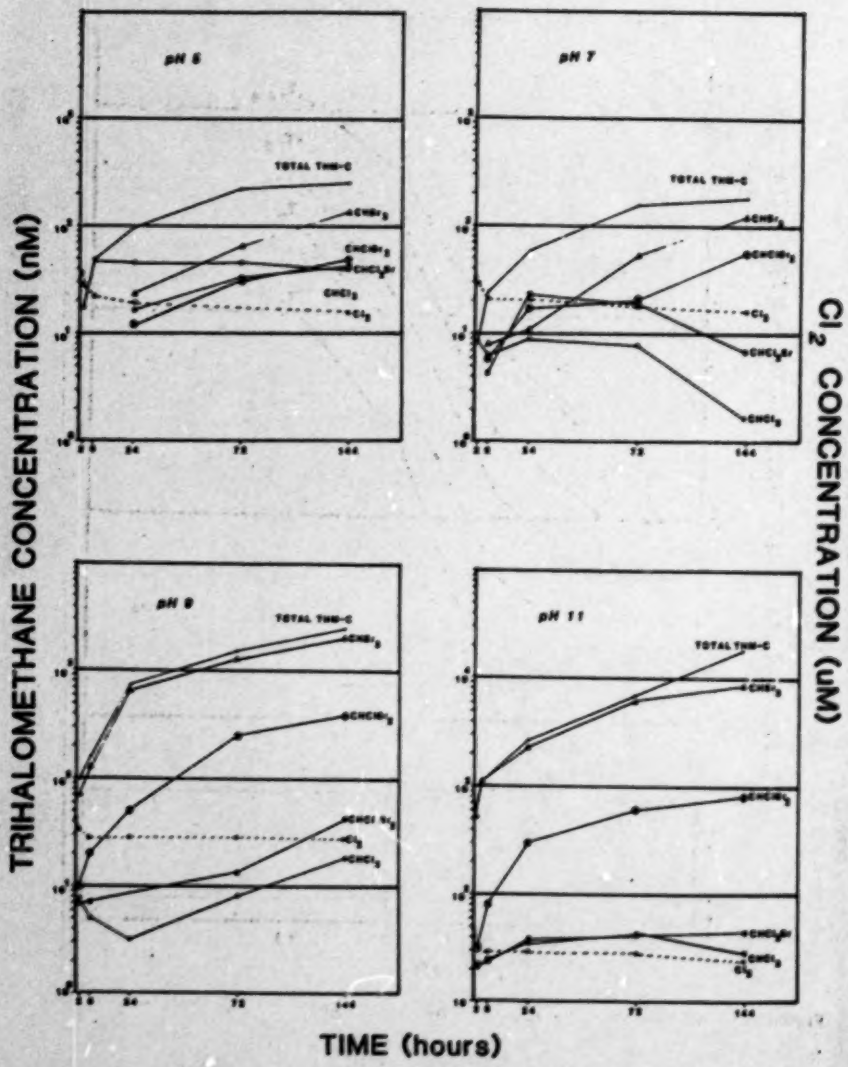


Figure 6. Trihalomethane formation at an α-methylbenzylamine/Cl_2 mole ratio of 1 and Br^- = 10^{-4} *M*.

increased with decreasing bromide concentration (Figure 8). From this it appears that the conversion of Br^- (inorganic) to THM-Br (organic bromine) increases both as a function of decreasing bromide and increasing pH. The apparent >100% conversion observed at pH 9 and 11 probably reflects the summation of errors in the THM measurements. Slight contamination by Br^-,

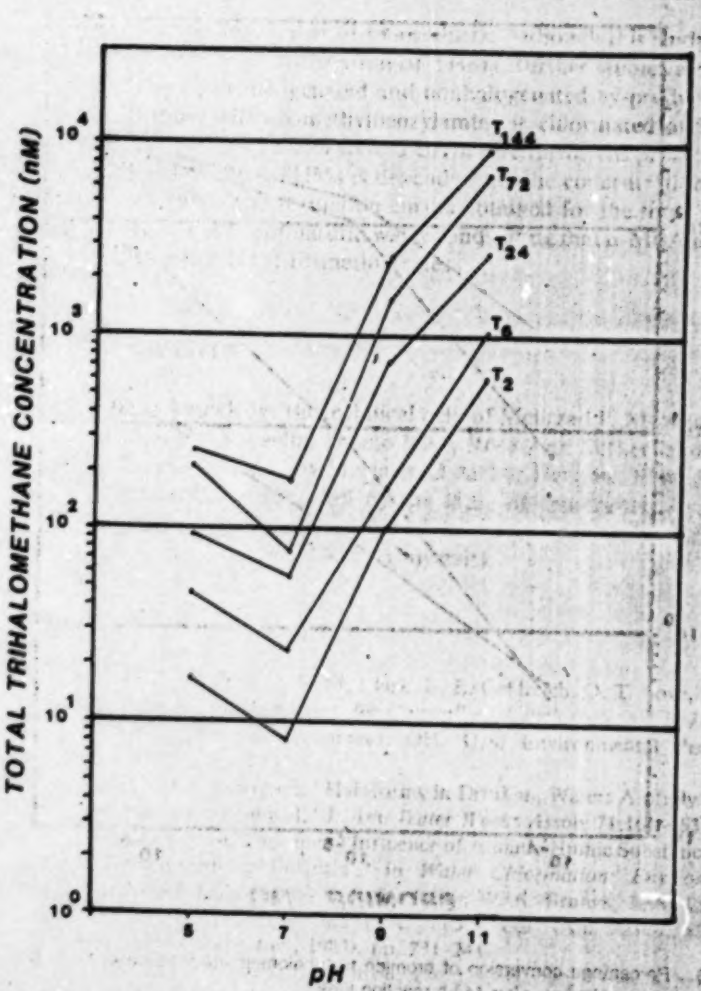


Figure 7. Total trihalomethane formation, Br^- = 10^{-4} *M*.

either in the chlorine-demand-free water or in the buffer reagents, is not the cause of the increase because when no bromide was added, only $CHCl_3$ was observed.

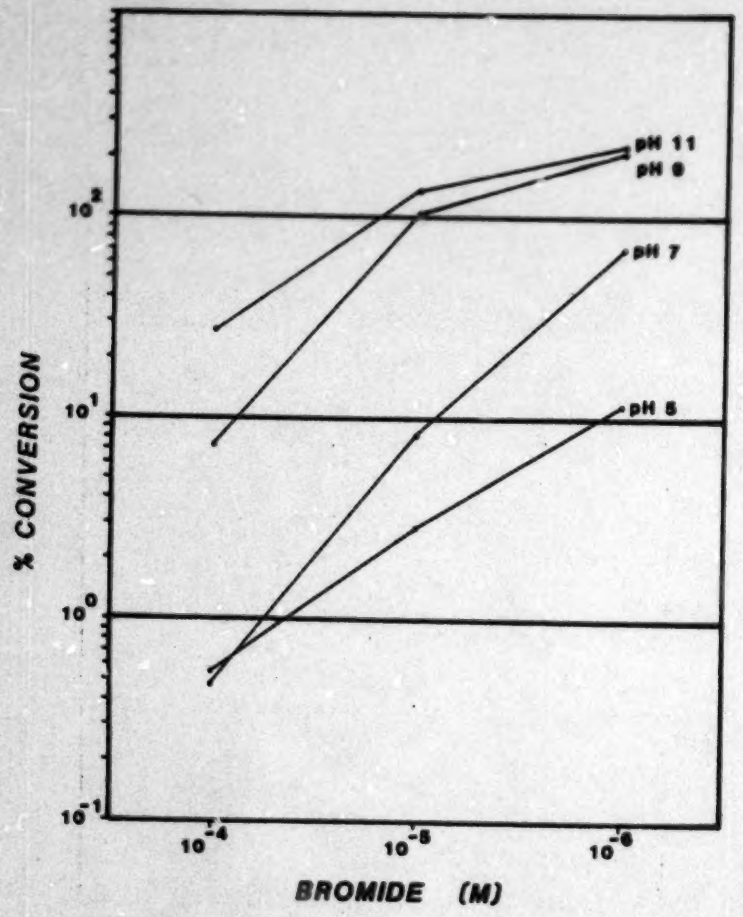


Figure 8. Percentage conversion of bromide to trihalomethane-bromine at three bromide concentrations, after 144-h reaction time.

SUMMARY AND CONCLUSIONS

A better understanding of the mechanisms and the factors affecting the formation and distribution of trihalomethanes in aqueous solution is needed if water treatment processes for controlling their formation are to be optimized. We have shown that α-methylbenzylamine is a good model compound for studying the formation and distribution of THMs. Advantages of using model compounds are more exact control of the concentration of the starting compounds and more detailed studies of by-products. Although this study reports only on the formation and distribution of THMs, further studies are in progress to determine other halogenated and nonhalogenated by-products.

THMs are formed when α-methylbenzylamine is chlorinated and, in the presence of Br^-, the mixed haloforms and $CHBr_3$ are formed as predicted. The formation of the individual THMs is dependent on the concentration of Br^-, pH, and reaction time. The formation curves obtained for the total THM as carbon closely follow those of natural waters, indicating that α-MBA is a good candidate for studying THM formation rates.

ACKNOWLEDGMENTS

We gratefully acknowledge the technical help of Mehrzad F. Mehran, Linda M. Meyer, Alessandra Vanzella, Duane Baur, Rose Ann Slifker, and Rafael Diaz and discussions with Daisey Macias and Arthur Herriott. Financial support for the research was provided by the U.S. Environmental Protection Agency Cooperative Agreement CR-810277-01 and the Drinking Water Research Center, Florida International University.

REFERENCES

1. Symons, J. J., A. A. Stevens, R. M. Clark, E. E. Geldreich, O. T. Love, Jr., and J. DeMarco. *Treatment Techniques for Controlling Trihalomethanes in Drinking Water.* EPA-600/2-81-156, (Cincinnati, OH: U.S. Environmental Protection Agency, 1981).
2. Oliver, B. G., and J. Lawrence. "Haloforms in Drinking Water: A Study of Precursors and Precursor Removal," *J. Am. Water Works Assoc.* 71:161–163 (1979).
3. Oliver, B. G., and E. M. Thurman. "Influence of Aquatic Humic Substance Properties on Trihalomethane Potential," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 4*, R. L. Jolley, W. A. Brungs, J. A. Cotruvo, R. B. Cumming, J. S. Mattice, and V. A. Jacobs, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 231–241.
4. Boyce, S., A. C. Barefoot, D. R. Britton, and J. F. Hornig. "The Formation of Trihalomethanes from Halogenation of 1,3-Dihydroxy-Benzenes in Dilute Aqueous Solution. The Synthesis of 2-^{13}C-Resorcinol and its Reaction with Chlorine and Bromide," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 4*, R. L. Jolley, W. A. Brungs, J. A. Cotruvo, R. B. Cumming, J. S. Mattice, and V. A. Jacobs, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 253–267.
5. Christman, R. F., J. D. Johnson, J. R. Hoss, F. K. Pfaender, W. T. Liao, D. L. Norwood, and H. J. Alexander. "Natural and Model Aquatic Humics: Raction with Chlorine," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 1*, R. L. Jolley, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1978), pp. 15–28.
6. Norwood, D. L., J. D. Johnson, R. F. Christman, J. R. Hoss, and M. J.

Bobenrieth. "Reactions of Chlorine with Selected Aromatic Models of Aquatic Humic Material," *Environ. Sci. Technol.* 14:187–189 (1980).

7. Rook, J. J. "Possible Pathways for the Formation of Chlorinated Degradation Products During Chlorination of Humic Acids and Resorcinol," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 3*, R. L. Jolley, W. A. Brungs, and R. B. Cumming, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980) pp. 85–98.
8. Onodera, S., M. Tabata, S. Suzuki, and S. Ishikura. "Gas Chromatographic Identification and Determination of Chlorinated Quinones Formed During Chlorination of Dihydric Phenols with Hypochlorite in Dilute Aqueous Solution," *J. Chromatogr.* 200:137 (1980).
9. Stevens, A. A. "Formation of Non-Polar Organo-Chlorine Compounds as Byproducts of Chlorination," in *Proceedings—Oxidation Techniques in Drinking Water Treatment, Sept. 11–13, 1978. Karlsruhe, F.R.G.*, EPA-570/9-79020 (Washington, DC: U.S. Environmental Protection Agency, 1979), pp. 145–160.
10. Boyce, S. D., and J. F. Hornig. "Reaction Pathways of Trihalomethane Formation from the Halogenation of Dihydroxyaromatic Model Compounds for Humic Acid," *Environ. Sci. Technol.* 17:202–211 (1983).
11. Boyce, S. D., and J. F. Hornig. "Formation of Chloroform from the Chlorination of Diketones and Polyhydroxybenzenes in Dilute Aqueous Solution," in *Water Chlorination: Environmental Impact and Health Effects, Vol. 3*, R. L. Jolley, W. A. Brungs, and R. B. Cumming, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980), pp. 131–140.
12. Boyce, S. D., and J. F. Hornig. "Reaction Processes Affecting the Analysis of Chloroform by Direct Aqueous Injection Gas Chromatography," *Water Res.* 17:685–697(1983).
13. Rook, J. J. "Chlorination Reactions of Fulvic Acids in Natural Waters," *Environ. Sci. Technol.* 11:478–482 (1978).
14. Morris, J. C., and B. Baum. "Precursors and Mechanisms of Haloform Formation in the Chlorination of Water Supplies," in *Water Chlorination: Environmental Import and Health Effects, Vol. 2*, R. L. Jolley, H. Gorchev, and D. H. Hamilton, Jr., Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1978), pp. 29–48.
15. Lee, G. A., and H. H. Freedman. "Phase Transfer Catalyzed Oxidations of Alcohols and Amines by Aqueous Hypochlorite," *Tetrahedron Lett.* pp. 641–44.
16. Guter, K. J., W. J. Cooper, and C. A. Sorber. "Evaluation of Existing Field Test Kits for Determining Free Chlorine Residuals in Aqueous Solutions," *J. Am. Water Works Assoc.* 66:38–43 (1974).
17. *Standard Methods for the Analysis of Water and Wastewater*, 15th ed. (Washington DC: American Public Health Association, 1980).
18. Cooper, W. J., M. F. Mehran, R. A. Slifker, D. A. Smith, J. T. Villate, and P. F. Gibbs. "Comparison of Several Instrumental Methods for Determining Chlorine Residuals in Drinking Water," *J. Am. Water Works Assoc.* 74:546–552 (1982).
19. Mehran, M. F., R. A. Slifker, and W. J. Cooper. "A Simplified Liquid-Liquid Extraction Method for Analysis of Trihalomethanes in Drinking Water," *J. Chromatogr. Sci.* 22:241–243 (1984).
20. Amy, G. L., P. A. Chadik, Z. K. Chowdhury, P. H. King, and W. J. Cooper "Factors Affecting the Incorporation of Bromide into Brominated Trihalomethanes During Chlorination," Chapter 71, this volume.